Modelling Internal Corrosion of High Temperature Alloys

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Outline

- What is Internal Corrosion?
- Wagner's Theory of Internal Oxidation
- Limitations of the Classical Theory
- Numerical Treatment of Internal Oxidation and Nitridation
  - Finite Difference
  - Cellular Automata
What is Internal Corrosion?

high-temperature corrosion: superficial scale + internal oxidation

selective oxidation

gas phase (O,N,S,C..)

metal oxide (AO) $D_{O/A}$

internal oxide (BO) $D_O$

alloy AB

metal oxide (BO) $D_O$

alloy AB
Transition from Internal to External Oxidation
Oxidation of Ni-Cr Alloys (100h, 1000°C, air)

depends on: $c_{Cr}/D_{Cr}/T$
Material Degradation by Internal Corrosion

gas and steam turbines, heat exchangers, chemical reactors, exhaust systems, metallurgy, heat treatment …

(Natural Gas Burner Tube, alloy 601)

internal nitridation (AIN)

500µm

superficial Cr₂O₃

internal Al₂O₃

internal AlN

30µm
Material Degradation during Cyclic Oxidation at 1100°C

- Al₂O₃ spallation
- Al depletion
- Transition to non-protective NiO
- Internal Al₂O₃/Cr₂O₃
- Internal AlN/TiN
- Cracks

Wedge-Shaped Specimen CMSX-4 at 1100°C
Carl Wagner's Theory of Internal Oxidation

Depth of the Internal Precipitation Zone $\xi$

$$\xi^2 = \frac{2c_O^s D_O}{Vc_B^0} t \quad \text{for} \quad \frac{D_B}{D_O} \ll \frac{c_O^s}{c_B^0} \ll 1$$

C. Wagner, Z. Elektrochemie, 21 (1959) 773
Carl Wagner's Theory of Internal Oxidation

Diffusion of O and B:

\[ c_O = c_O^0 \left(1 - \frac{\text{erf}(x/2\sqrt{D_O t})}{\text{erf} \gamma}\right) \]

\[ c_B = c_B^0 \left(1 - \frac{\text{erfc}(x/2\sqrt{D_B t})}{\text{erfc} \left(\gamma \sqrt{D_O / D_B}\right)}\right) \]

Mass Balance at \( \xi \):

\[-D_O \left(\frac{\partial c_O}{\partial x}\right)_{x=\xi-\varepsilon} = vD_B \left(\frac{\partial c_B}{\partial x}\right)_{x=\xi+\varepsilon} \]

Depth of the Internal Precipitation Zone \( \xi \)

\[ \xi^2 = \pi \frac{D_O^2}{D_B} \left(\frac{c_O^s}{v c_B^0}\right)^2 t \quad \text{for} \quad \gamma \ll 1 \quad \gamma \sqrt{\frac{D_O}{D_B}} \ll 1 \]

C. Wagner, Z. Elektrochemie, 21 (1959) 773
Carl Wagner's Theory of Internal Oxidation

Mass Balance:
Mole fraction $BO_v \leftrightarrow \text{B flux to reaction front}$

$$\frac{fA d\xi}{V_m} = \left[\frac{AD_B}{V_m} \frac{\partial c_B}{\partial x}\right] dt$$

Transition from Internal to External Oxidation

$$c_B^0 > \pi \left[\frac{\pi g^*}{2V} c_O^s \frac{D_O V_m}{D_B V_{Ox}}\right]$$

with $g^*$: crit. volume fraction of oxide

C. Wagner, Z. Elektrochemie, 21 (1959) 773
Limitations of Wagner's Analytical Approach

One type of precipitates of high thermodynamic stability (solubility product \( K_{SP} = N_B N_0^\gamma \approx 0 \))

Constant boundary conditions - no changes in temperature, gas composition etc. possible

Effective diffusivity - through complex microstructure, e.g., \( D_{GB} > D_{bulk} \)

One-dimensional - nucleation and growth kinetics / changes in the diffusion path are neglected
Nucleation and Growth of Internal Precipitates
(TiN and AlN in NiCr20Al2Ti2, 1000°C, 150h, N₂)

Energy Balance:
interface energy $\gamma$
free energy change $\Delta G$
strain energy $\Delta G_s$
(defect site annihilation energy)

$$\Delta G = V(\Delta G_v + \Delta G_s) + \sum_i A_i \gamma_i$$

Supersaturation

G. Böhm, M. Kahlweit, Acta Met., 12 (1964) 641
Finite-Difference Treatment of Diffusion

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

\[ \left( \frac{\partial c}{\partial t} \right)_{x,t} \approx \frac{c(x, t + \Delta t) - c(x, t)}{\Delta t} \]

\[ \left( \frac{\partial^2 c}{\partial x^2} \right)_{x,t} \approx \frac{c(x + \Delta x, t) - 2c(x, t) + c(x - \Delta x, t)}{\Delta x^2} \]

\[ c_i(x, t + \Delta t) = c(x, t) + \frac{D\Delta t}{\Delta x^2} \left[ c(x - \Delta x, t) - 2c(x, t) + c(x + \Delta x, t) \right] \]
Finite-Difference Treatment of Diffusion

$$c(x, t + \Delta t) = c(x, t) + \frac{D\Delta t}{\Delta x^2} \left[ c(x - \Delta x, t) - 2c(x, t) + c(x + \Delta x, t) \right]$$

computational thermodynamics
ChemApp + system data
(GTT technologies)

$$G = \sum_{j=1}^{m} c_j \left( G_{j,\text{pure}} + G_{j,\text{id}} + G_{j,\text{non-id}} \right)$$

= min !
2D Finite-Difference Treatment of Diffusion
(Crank Nicolson implicit approach)

\[
D = f(x, y)
\]
(e.g. PVM)

bulk and gb diffusion

Parallelization
(e.g. PVM, GPU/CUDA)

ChemApp / system
data base initialisation
distributed equilibrium
calculations

C – Main program
FD diffusion calculation
user interface

Finite-Difference Simulation of Internal Precipitation of Cr-Nitrides of Moderate Stability (NiCr20, 800°C, N₂)
Oxidation of Low-Cr Steels (X60)
(1.43wt% Cr, 550°C, air)
2D Simulation of Internal Oxidation

Fe₃O₄/FeCr₂O₄
inner oxide scale thickness
grain boundaries

FeCr₂O₄
Inner Oxide-Scale Growth (X60)

(1.43wt% Cr, 550°C, air)
The Cellular Automata Approach

Dividing Space into Lattice

Defining a Neighbourhood
(von Neumann, Moore)

Defining State Variables
(e.g.: 0,1)

Defining Transition Rules
(applied simultaneously to all cells)

The Cellular Automata Approach (Chopard and Droz)

Probabilities

\[ p_1 = p_3 = p \]
\[ p_0 + 2p + p_2 = 1 \]

Diffusion Coefficient

\[
D_N = \frac{\lambda^2}{\tau} \left( \frac{1}{4(p + p_2)} - \frac{1}{4} \right) = \frac{\lambda^2}{\tau} \left( \frac{p + p_0}{4(1 - p - p_0)} \right)
\]

with

\[ \lambda = \frac{X}{n_x}, \tau = \frac{T}{n_t} \]

Chopard and Droz, Cellular Automata Modeling of Physical Problems, Cambridge Univ. Press 1998
Diffusion Profile (Chopard and Droz)

The analytical solution for the diffusion profile is given by:

$$ c(x,t) = c_s \left(1 - \text{erf} \left( \frac{x}{2 \sqrt{D t}} \right) \right) $$

where $c(x,t)$ is the concentration at location $x$ and time $t$, $c_s$ is the initial concentration, $D$ is the diffusion coefficient, and $t$ is time.
The Cellular Automata Approach for Internal Precipitation (Zhou and Wei)

Initialization

Diffusion: N stepwise to the right
B every 20th iteration to the left

Transition: B+N=>BN:
(Implementation ChemApp possible)

solvent: inert (I)
solute: active element (B)
nitride (BN)
nitrogen (N)
The Cellular Automata Approach
for Internal Precipitation (Zhou and Wei)

Stable state (AN)

Transition $p_T$:

Transition $p_T^r$:

Zhou and Wei, Scripta Mater., 37 (1997) 1483
Internal Precipitation (Zhou and Wei) + N- Diffusion (Chopard and Droz)

(location y) (arbitrary units)

512 x 512 cells
20000 iterations

(location x) (arbitrary units)

512 x 512 cells
1500 iterations

(increased B counter diffusion)
Precipitation + N Diffusion (Chopard and Droz) + B Diffusion in the Internal Precipitation Zone

- solvent (inert)
- active element B
- nitride (BN)

Nitride sink (min 5 nitrides within R=5 cells)
Precipitation + B Diffusion in the Internal Precipitation Zone – Concentration Profile

concentration (cells / 512cells)

Figure: Concentration profile of nitride BN and active element B. The concentration is plotted against location x (10^-6 m). The nitride BN shows a higher concentration compared to the active element B.
Precipitation + B Diffusion in the Internal Precipitation Zone – Penetration Depth

penetration depth $\xi$ [µm]

(Ni-20Cr-6Ti 1000°C, $N_2$)

incubation time: non-stable precipitates

square root of exp. time [$h^{-0.5}$]
Grain boundary diffusion

\[ D_{GB} > D_{bulk} \]

512 x 512 cells
3000 iterations
\( T_{tot} = 100h, \ T = 800\, ^\circ C \)
Conclusions and Future Aspects

- Classical Wagner theory is limited to special scenarios
- Finite Difference: easy combination with ChemApp
- Cellular Automata:
  - nucleation and growth
  - 3D effects: various diffusion paths (e.g., GB/bulk diffusion)
- Problems to be solved:
  - combination of small and large concentrations
  - implementation of ChemApp

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